

Alkyl Pyrocarbonate Electrolyte Additives for Performance Enhancement of Li ion cells

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Lithium ion rechargeable batteries are being developed for various aerospace applications under a NASA-DoD interagency program. These applications require further improvements in several areas, specifically in the cycle life for LEO and GEO satellites and in the low temperature performance for the Mars Lander and Rover missions. Accordingly, we have been pursuing research studies to achieve improvements in the low temperature performance, long cycle life and active life of Li ion cells. The studies are mainly focused on electrolytes, to identify newer electrolytes formulations or new electrolyte additives to enhance Li permeability (at low temperatures) and stability towards the electrode. The latter approach is particularly aimed at the formation of suitable SEI (solid electrolyte interphase) on carbon electrodes. In this paper, we report the beneficial effect of using alkyl pyrocarbonates as electrolyte additives to improve the low temperature performance of Li ion cells.

The use of pyrocarbonate additives to the electrolyte has been mentioned briefly in the literature.¹ These additives generate *in-situ* either CO₂ or lithium oxygenated species, via decomposition, which would aid in the formation of suitable SEI on graphite.

Our recent studies on the low temperature electrolytes have led to several electrolyte formulations, i.e., a ternary, equi-proportion mixture of EC, DMC and DEC^{2a}, and quaternary solvent mixtures using aliphatic esters and asymmetric alkyl carbonates as quaternary components to the EC:DEC:DMC solvent mixtures.^{2b} We report here the beneficial effects of alkyl pyrocarbonate additives to some of these solvent mixtures on the (low temperature) performance and stability of lithium ion cells. We have studied the effects of two pyrocarbonate additives, i.e., dimethyl pyrocarbonate and dibutyl pyrocarbonate, in varying amounts (5 and 25 vol%)

Since the intent of these studies is to assess the characteristics of SEI, such as Li ionic resistance, ease of Li intercalation across the interface especially at low temperatures, and the stability of the film during storage, we have fabricated Li-carbon (MCMB) half-cells with electrolytes varying in the pyrocarbonate type, and solvent composition. The electrolytes chosen for these studies are :

- 1) 1.00 M LiPF₆ EC+DEC+DMC (1:1:1)
- 2) 0.75 M LiPF₆ EC+DEC+DMC+ DMPC (1:1:1:1)
- 3) 0.95 M LiPF₆ 5% DMPC in the baseline (1)
- 4) 0.95 M LiPF₆ 5% DBPC in the baseline (1) and
- 5) 0.75 M EC+DEC+DMC+EA+DBPC (5:5:5:4:1)

Various basic electrochemical studies were performed on these cells to determine the reversible and irreversible capacities, Li intercalation/ deintercalation kinetics at low temperatures and during storage.

The reversible capacity was found to be higher with 5 vol% pyrocarbonate content, compared to solutions with 25 vol% or the baseline formulation. At low temperatures, on the other hand, solutions containing the di-*t*-butyl pyrocarbonate additives displayed the best

performance (Fig. 1), suggesting that the DBPC additive produces a superior surface film on carbon allowing rapid lithiation kinetics at low temperatures.

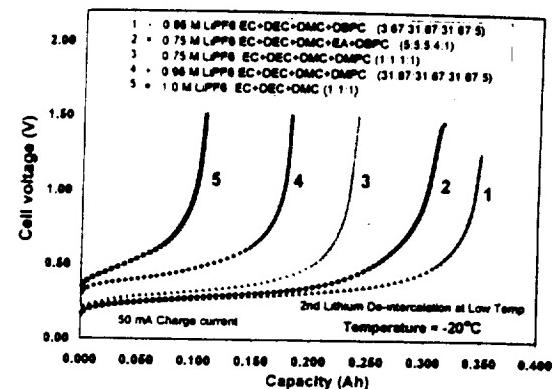


Fig. 1. Li de-intercalation in different electrolytes at -20°C, preceded by intercalation at low temperature.

The superior low temperature performance in solutions with pyrocarbonate additives is further substantiated by the EIS measurements. The resistance of the SEI is significantly lower in solutions containing pyrocarbonate additives both at ambient and low (Fig.2) temperatures.

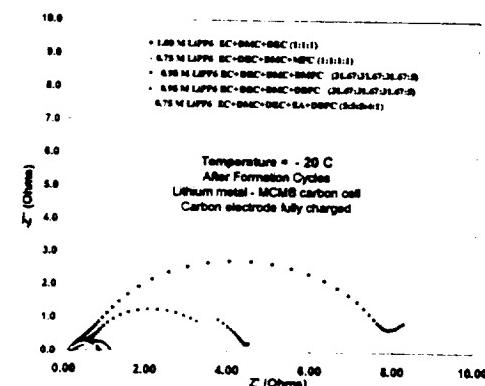


Fig. 2: EIS plots of graphite anode in electrolytes with and without pyrocarbonate additives at -20°C.

These observations of improved SEI characteristics and enhanced Li intercalation/deintercalation kinetics, especially at low temperatures, are further corroborated by Dc polarization, i.e., micropolarization and Tafel measurements.

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References

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